

## UNITED STATES PATENT OFFICE

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## METAL PLATING PROCESS

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1 Claim. (Cl. 117—130)

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This invention relates to new compositions of matter useful in the commercial production of metal plating. More particularly the invention comprises metal salts of hydroxythiols, their aqueous solutions, metal plating baths containing such salts, and the process of metal plating from solutions containing metal salts of hydroxythiols.

The art of metal plating is one of great industrial importance and methods for improving the efficiency and quality of metal plating have long been sought. Metal plating may be carried out by electrodeposition in which the object to be plated is made the cathode of an electrolytic cell and the electrolyte used is a salt of the metal to be plated. Metal coatings may also be obtained by immersion plating in which the object to be plated is immersed in a bath containing a salt of the plating metal.

This invention has as an object the preparation of new compositions of matter useful in the commercial production of metal plating. Another object is to provide an improved metal plating bath containing new metal compounds. A still further object is to provide a new and improved method of metal plating by means of which dense, bright, and adherent metal coatings are obtained. Other objects will appear hereinafter.

We have now found that new compositions of matter comprising metal salts of hydroxythiols are well suited for use in metal plating processes. When metal salts of hydroxythiols are used as the principal ingredient, in plating baths, excellent coatings are obtained which are dense, bright, and adherent. These baths are easy to prepare and may be utilized in conventional plating operations.

Hydroxythiols are a class of organic compounds which may be prepared readily and economically as described in United States patent application Serial No. 357,417, filed September 19, 1940. This method of preparation consists essentially of catalytically hydrogenating a hydroxycarbonyl compound in the presence of hydrogen sulfide. A class of hydroxycarbonyl compounds which lend themselves very satisfactorily to the preparation of hydroxythiols by this procedure and which are in many instances available in quantity and at low cost are the reducing sugars.

We have discovered that hydroxythiols unite with many metals to form soluble compounds useful for plating. Members of the class of hydroxythiols derived from reducing sugars possess

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the additional advantage of being very soluble in water, a property which is also exhibited by their metal salts.

Our invention consists in new compositions of matter comprising metal salts of hydroxythiols and their preparation, their aqueous solutions, plating baths containing metal salts of hydroxythiols, and the process of plating from baths containing metal salts of hydroxythiols.

In practicing this invention a metal salt of a polyhydroxythiol may be prepared readily by dissolving a metal oxide or hydroxide preferably in freshly precipitated or finely dispersed form in an aqueous solution containing an equivalent amount of polyhydroxythiol. When necessary, heat is employed to assist the reaction. Alternatively, a metal salt, preferably of a non-oxidizing acid, may be dissolved in an aqueous solution of a polyhydroxythiol or the thiol added to an aqueous solution or suspension of the metal salt. If the metal stands low in the electromotive series of metals then the acid corresponding to the negative radical of the salt will be liberated. This acid, if volatile, may be separated from the metal salt of the hydroxythiol by evaporating the resulting solution or the acid may be neutralized with an equivalent amount of alkali to yield a neutral solution of the metal salt of the hydroxythiol. The metal salts of polyhydroxythiols may be isolated by evaporating their aqueous solutions to dryness but it is preferable first to prepare the salt by a procedure in which the use of water as solvent is avoided. When a polyhydroxythiol is soluble in acetic acid, any of its salts may be precipitated by adding a solution of the selected metal acetate in acetic acid. If the polyhydroxythiol dissolves in an alcohol, a metal alcoholate may be employed to precipitate the salt.

While a simple solution of a metal salt of a hydroxythiol may be used as plating solution, it is generally preferred to have other compounds present in the solution. For example, the rate of plating (i. e., amount of metal plated out in a given time) generally may be increased by the presence of a mineral acid, such as hydrochloric or sulfuric acid. In most cases an acid concentration equivalent to 1 to 10% by weight of sulfuric acid is satisfactory. It has been observed that hydroxythiols greatly inhibit the corrosion of iron by mineral acids and thus permit the use of a considerable amount of mineral acid in the solution without causing excessive corrosion of the metal base to be plated. In preparing a plating solution of a metal salt of a hydroxythiol, a

mineral acid may be added to the neutral salt or the acid-containing solution may be prepared by dissolving the metal salt of the acid in the hydroxythiol solution as described in the preceding paragraph. Further, the acid concentration of a solution so prepared may be adjusted to the desired value by the addition of mineral acid or alkali. Soluble salts of the metal to be plated also may be added to the hydroxythiol salts, e. g. sulfates, chlorides, double cyanides and the like.

In the operation of plating from baths containing metal salts of hydroxythiols, as in nearly all plating operations, it is essential that the object to be plated first be cleaned by suitable means to free the surface of oxides, grease, etc. While it is desirable that oxide films be first removed from the metal objects, the hydroxythiols dissolve metallic oxides and to some extent can be employed for this purpose in the plating solution.

The operation of plating by immersion is carried out in conventional manner, i. e., simply by suitably contacting the object to be plated with the plating solution, which may or may not be heated, depending upon the rate of deposition desired. If the baths are used for electrodeposition of a metal, in most cases they may be continuously regenerated by anodic solution of the metal plated, as in conventional electroplating practice.

The hydroxythiol may be recovered from spent baths, for example, by precipitating the metal with hydrogen sulfide followed by filtration to remove the metal sulfide. The resulting aqueous solution of the free hydroxythiol, after removal of excess hydrogen sulfide may then be used for preparing a new bath.

Among the hydroxythiols which may be used in this invention, the polyhydroxythiols containing one or more primary or secondary mercapto groups are preferred because of the greater solubility of their metal salts in water. A further preferred class of hydroxythiols for use in this invention are the polyhydroxythiols having a hydroxyl group on a carbon atom in the alpha or beta position with respect to a carbon atom bearing a mercapto group.

Examples of the polyhydroxythiols suitable for the practice of this invention are those which are derived by catalytic hydrogenation in the presence of hydrogen sulfide of reducing sugars, particularly the aldo- and keto-hexoses, such as glucose (dextrose), mannose, galactose, fructose, and sorbose, or disaccharides such as sucrose, maltose, lactose, and cellobiose. Specific examples of suitable polyhydroxythiols are the pentahydroxyhexanethiols, such as 1-thiosorbitol, 2-thiosorbitol, thiomannitol, thiodulcitol; the tetrahydroxyhexanethiols, such as thiorhamnitol; the tetrahydroxypentanethiols, such as thioxylitol; trihydroxybutanethiols, such as thioerythritol; and thiopentaerythritol.

The metal salts of polyhydroxythiols are new compositions of matter and as such are a part of this invention. They include generally the salts of all of the metals with polyhydroxythiols, i. e., both the plating metals and the nonplating metals. More specifically, there are included salts of the alkali metals, as for example sodium and potassium; alkaline earth metals, such as calcium, barium, magnesium; other light metals such as aluminum, zinc; and the ferrous metals, heavy metals and noble metals. The metal salts of polyhydroxythiols, especially those having three or more hydroxyl groups are readily water soluble.

Moreover, the salts of the heavy metals are but little ionized in solution. We have found that in general the tendency of the metal salts of polyhydroxythiols to undergo ionization in aqueous solution corresponds roughly to the position of the metal in the electromotive series of metals, salts of the metals standing low in the electromotive series being the less ionized.

While generally we prefer to utilize in the practice of this invention the polyhydroxythiols, as illustrated by the above examples, our invention is not restricted thereto; but we may utilize for plating a metal, a soluble salt of that metal and any hydroxythiol. That is, the hydroxythiols suitable for our purpose are those which form soluble salts of the metals to be plated.

In practicing this invention it is generally unnecessary to isolate the metal salts of the hydroxythiols as the crude solution obtained by dissolving the metal or metal compound in the aqueous polyhydroxythiol ordinarily is suitable for use in the plating operation. For example, the crude aqueous solutions obtained by the hydrogenation of reducing sugars in the presence of hydrogen sulfide can be so used. While in the preparation of the metal salts of hydroxythiols it is only necessary to use stoichiometric equivalents of the reactants, an excess of the hydroxythiol is generally not harmful and in some cases may be advantageous. When the metal salt used as a reactant is capable of oxidizing the hydroxythiol to the disulfide, as for example cupric salts, one equivalent of hydroxythiol is so consumed and the complex salt subsequently formed is that of the metal in a reduced state. In such cases the hydroxythiol so lost may be recovered when the bath is regenerated by reduction of the disulfide either catalytically with hydrogen or by appropriate chemical reagents.

Our plating process is generally applicable to all the plating metals, particularly those standing below calcium in the electromotive series of metals. By "plating metals," we mean any metals or alloys thereof which can be plated from aqueous solutions onto metal or other electrically conductive bases to produce metallic coatings. Specific examples of such metals which may be plated from baths containing the polyhydroxythiol salts of these metals are: cadmium, chromium, nickel, cobalt, copper, gold, iron, lead, platinum and the other metals of the platinum group, silver, tin, zinc, and manganese.

In employing baths containing metal salts of hydroxythiols for plating, it is frequently desirable to modify these baths in such a manner that the metal ion concentration is greater than that normally yielded by the salt alone. This object may be accomplished as explained above, for example by the addition of sulfuric acid, or other substantially nonoxidizing acids, such as hydrochloric acid or phosphoric acid. Oxidizing acids, such as nitric acid, which would oxidize or destroy the complex salt are not suitable. The amount of non-oxidizing mineral acid to be so used will depend to a great extent upon the particular metal used and the other conditions of the plating operation. A preferred concentration of acid will in general be found within the range between 1 and 10 per cent.

While we prefer to use acids in the plating baths, as above described, we may add, in conjunction with, or in place of acids, salts containing anions which form soluble salts with the metals plated. Such salts include, for example, soluble sulfates, chlorides, phosphates and cya-

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nides. Such soluble salts may be simple or complex salts of the plating metals, or they may be soluble salts of non-plating metals such as the alkali or alkaline earth metals, e. g., sodium sulfate, sodium cyanide, etc.

This invention is further illustrated by the following examples, in which the quantities involved are expressed in parts by weight:

#### Example I

An aqueous solution of copper sulfate is prepared by dissolving 10 parts of copper sulfate pentahydrate in 50 parts of water. To this solution is added slowly with stirring an aqueous solution of 1-thiosorbitol (a polyhydroxythiol) prepared by dissolving 13 parts of solid 1-thiosorbitol in 50 parts of water.

As the solution is added, readily perceptible color changes occur, the mixed solutions changing from blue to green and finally to yellow or orange in color. The resulting solution is diluted by adding 100 additional parts of water; and 5 parts of sulfuric acid (specific gravity 1.8) is added. The acidified solution should be used immediately or stored in a container out of contact with air, since the cuprous salt present otherwise undergoes slow oxidation to the cupric state.

A steel object is cleaned to free it of scale, oxide, and grease by brushing with a solution of phosphoric acid in methanol, washed and immersed in the plating bath which has been heated to 60–80° C. A dense, adherent coating of copper is deposited and after a period of time, which may be predetermined for the thickness desired, the object is removed and washed with water.

#### Example II

An aqueous solution of 6 parts of 1-thiosorbitol dissolved in 100 parts of water is warmed to 70–90° C. and 4 parts of cuprous oxide added with agitation until solution of essentially the entire amount is effected. The resulting yellow solution is diluted with 100 parts of water and filtered if necessary. The bath is prepared for use as in Example I by adding 5 parts of sulfuric acid and warming to 60–80° C.

#### Example III

Sixty-five parts of commercial dextrose and 30 parts of powdered sulfur are charged into a hydrogenation autoclave together with 100 parts of water and 8 parts of a cobalt sulfide catalyst prepared by precipitating an aqueous solution of 13 parts of cobalt chloride hexahydrate with a solution of 16 parts of sodium polysulfide. Hydrogen is admitted to the autoclave to a pressure of 1500 lbs./sq. in. and the autoclave is agitated and heated to a temperature of 125° C. As reaction ensues additional hydrogen is admitted from time to time to maintain the pressure within the range from 1300 to 1900 lbs./sq. in. Although hydrogen is absorbed only slowly after the first hour, the autoclave is heated for an additional two to three hours to insure completion of the reaction. The autoclave is cooled and the product is rinsed out with water and filtered to separate the catalyst.

The aqueous solution is heated at 100° C. under a pressure of 10–15 mm. to remove substantially all the water and steam volatile impurities. The product consisting of fifty-three parts of a viscous syrup is redissolved in about an equal amount of water and the 1-thiosorbitol content

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of this solution is estimated volumetrically with standard iodine solution.

Thirty parts of this solution which corresponds to 13 parts of 1-thiosorbitol is added with stirring to a solution of 10 parts of copper sulfate pentahydrate in 150 parts of water. To the resulting solution 5 parts of sulfuric acid is slowly added with stirring.

The solution is warmed to 80° C. and poured into a section of steel pipe previously cleaned by pickling with acid and closed at one end. After 10 minutes the solution is removed and the inner wall of the pipe is flushed with water. A smooth, adherent lining of copper is so obtained.

The plating baths described in the preceding examples, as well as others containing metal salts of hydroxythiols, may be used advantageously for electrodeposition to produce bright, adherent coatings of good quality. Heated baths are generally unnecessary for the electrodeposition.

#### Example IV

This example illustrates an electroplating operation with a bath containing a metal salt of hydroxythiols. A plating bath is prepared by treating an aqueous solution of 10 parts of copper sulfate pentahydrate in 50 parts of water with 50 parts of an aqueous solution containing 13 parts of 1-thiosorbitol and diluting the resulting solution with an additional 100 parts of water.

An object of lead or a high lead alloy is cleaned by buffing and made the cathode while a platinum object conveniently serves as the anode. The ratio of anode to cathode surface is preferably greater than one. The current density is adjusted soon after the start to 0.6 amp./dm.<sup>2</sup>. Copper is deposited and hydrogen is evolved simultaneously at the lead cathode. The coating deposited is more or less bright, depending on the preliminary buffing of the lead object.

It is possible in the above manner to deposit other metals, such as nickel, tin, or silver from baths similarly prepared.

#### Example V

An alkaline nickel plating bath is prepared by dissolving 50 parts of sodium nickel cyanide ( $\text{Na}_2\text{Ni}(\text{CN})_4$ ) in water at 60° C., adding an aqueous solution of 10 parts of potassium hydroxide and stirring to effect complete solution of any solids; then adding 50 parts of thiosorbitol in 30% aqueous solution and diluting with water to a concentration equivalent to 50 grams per liter of thiosorbitol.

The solution is electrolyzed with a polished steel cathode and an anode of electrolytic nickel, at current densities of 18 amps. per sq. ft. at the cathode and 10 amps. per sq. ft. at the anode. The resulting electrodeposit is ductile and bright, having a brightness equal to that of the polished steel cathode and has excellent adherence. Equally good results are obtained by plating at bath temperatures of 30° C. and 70° C. The nickel anode readily dissolves to replenish the bath with nickel, there being no indication of anode polarization which usually occurs in alkaline nickel plating baths.

#### Example VI

An unusual example is provided in the immersion plating of tin on copper without the use of contact metals. A solution of 6 parts of 1-thiosorbitol in 100 parts of water is warmed to 60–80° C. and 3 parts of stannous chloride added.

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The resulting slightly turbid solution is filtered and added to a solution of 25 parts of sodium cyanide in 400 parts of water.

Objects of copper or brass and other objects having a base plate of copper acquire a bright coating of tin when immersed in the solution so prepared. The hydroxythiol provides in this instance a slightly ionized, water soluble tin salt for use where simple tin salts are entirely unsuitable due to their tendency to undergo hydrolysis and precipitate.

The following examples relate to the preparation of aqueous solutions of a number of metal salts of thiosorbitol and also to the isolation of several of the metal salts of thiosorbitol and serve to illustrate the preparation of metal salts of hydroxythiols.

#### Example VII

Aqueous solutions of metal salts of 1-thiosorbitol were prepared by dissolving in an approximately equivalent amount of 1-thiosorbitol in the form of a 25% solution in water, the following freshly precipitated metal oxides or hydroxides:

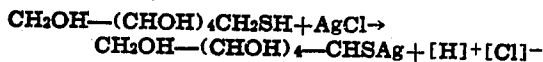
Zinc hydroxide → zinc salt of 1-thiosorbitol  
Cupric hydroxide → copper salt of 1-thiosorbitol  
Cuprous oxide → copper salt of 1-thiosorbitol  
Ferric hydroxide → iron salt of 1-thiosorbitol  
Lead hydroxide (or oxide) → lead salt of 1-thiosorbitol  
Mercuric hydroxide (or oxide) → mercury salt of 1-thiosorbitol  
Silver hydroxide (or oxide) → silver salt of 1-thiosorbitol

#### Example VIII

Acidic solutions of metal salts of 1-thiosorbitol were prepared by dissolving in an approximately equivalent amount of 1-thiosorbitol in the form of a 25% solution in water, the following metal salts:

Silver chloride → silver salt of 1-thiosorbitol + HCl  
Silver iodide → silver salt of 1-thiosorbitol + HI  
Lead iodide → lead salt of 1-thiosorbitol + HI  
Cuprous chloride → cuprous salt of 1-thiosorbitol + HCl  
Mercuric chloride → mercury salt of 1-thiosorbitol + HCl  
Stannous chloride → stannous salt of 1-thiosorbitol + HCl

The formation of the salts with the liberation of the corresponding free acid reveals the non-ionic character of the heavy metal salts of polyhydroxythiols. The reaction may be represented as follows:



#### Example IX

To an aqueous solution of 1-thiosorbitol, aqueous ammonium hydroxide is added in equal molecular amount. The resulting solution of the ammonium salt of 1-thiosorbitol is shaken with an equivalent amount of powdered lead chromate. The lead chromate immediately dissolves, forming a solution of the lead salt of 1-thiosorbitol.

#### Example X

A solution of 10 parts of 1-thiosorbitol in 25 parts of glacial acetic acid is prepared by heating until the 1-thiosorbitol is completely dissolved and the solution then cooled to room temperature. To this is added with shaking a solution of 7

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parts of mercuric acetate in 25 parts of acetic acid. The precipitated mercuric salt is collected on a funnel and washed with 25 parts of acetic acid and then with sufficient anhydrous ether to substantially free the precipitate of acetic acid. The salt contained 9.0% sulfur.

#### Example XI

Fifty parts of 1-thiosorbitol is dissolved in 100 parts of absolute ethanol with heating and the solution then cooled out of contact with air to 10–15° C. A cooled solution of sodium ethylate obtained by dissolving 6 parts of sodium in absolute ethanol is added dropwise to the well agitated 1-thiosorbitol solution. The sodium salt of 1-thiosorbitol separates as a bulky white solid. This is collected on a funnel by suction out of contact with moist air and washed with absolute alcohol and then ether. It is dried in vacuo.

#### Example XII

Forty parts of 1-thiosorbitol is dissolved in 50 parts of water and 8 parts of calcium hydroxide added. The solution is warmed to 60–70° C. and shaken to effect solution of the calcium hydroxide. After thirty minutes the solution is allowed to cool and stand overnight. The undissolved calcium hydroxide is separated by filtration and the clarified solution then concentrated under reduced pressure to remove the water solvent. The viscose product is covered with about an equal volume of absolute ethanol and stirred until the calcium salt is obtained as a hard, granular solid. It is collected on a funnel protected from moist air, washed with absolute ethanol and anhydrous ether and dried in vacuo.

The foregoing examples relate to the preparation of specific metal salts of hydroxythiols and their use in plating baths. However, this invention is applicable to a variety of similar salts by employing other hydroxythiols which form water soluble metal salts in the manner described herein.

In the examples, we have described specifically the plating of copper and tin from baths containing the polyhydroxythiol salts of these metals onto iron and steel and lead objects. However, the process of this invention may be used similarly to plate the same or other metals onto other base metals or conducting materials. For example, ordinary forms of mild iron may be plated and also ordinary steel and stainless steels. Other metallic bodies which may be so plated include those made of brass, copper, silver, and the various commercial alloys, both ferrous and nonferrous. In addition, this invention is applicable to the deposition of metal coatings on nonmetal objects which may be first coated with a metal conductor by means of sputtering or other techniques. Similarly objects made of graphite or coated with graphite may be plated by the process of this invention.

The herein described metal salts of polyhydroxythiols, which are new compositions of matter, are particularly useful for the formation of baths for immersion deposition or electrodeposition of metals. The use of such baths for metal plating produces dense, adherent coatings having protective and decorative value. The addition of hydroxythiols to electroplating baths, and especially the polyhydroxythiols, insures adequate and uniform corrosion of the anodes under all conditions.

Metal salts of hydroxythiols may also be used for plating operations in conjunction with the conventional cyanide baths where the application

of successive metal coatings is advantageous. They may also be used in certain cases to modify cyanide plating baths in order to secure improved coatings. Likewise, hydroxythiols may be added to other conventional plating solutions, acid or alkaline, to obtain improved results, e. g., to baths containing sulfates, chlorides, cyanides or other soluble salts of plating metals. In modifying metal plating electrolytes, we generally prefer to add at least 10% by weight of the hydroxythiol, usually around 40 to 60%, so as to form a substantial concentration of the hydroxythiol salt of the metal plated.

A particular advantage of our plating process is that it may be employed to deposit metallic coatings on difficultly accessible surfaces, such as recessed parts or the inner walls of hollow objects, as for example pipes or tubing. This process also may be used to advantage in conjunction with acid-copper plating, as it may be employed to provide the necessary flash coating of copper prior to electrodeposition from acid baths. In the electrowinning of metals from solutions of their salts, the quality of the recovered metal can be improved by first converting the simple salts to complex salts of hydroxythiols.

The metal salts of hydroxythiols are effective

for metal plating under a wide range of conditions of concentration, temperature, current density, etc. The optimum conditions must be determined however for each particular type of plating operation, as will be evident to those skilled in the art.

The salts of monothiol sugar alcohols of at least five carbon atoms and particularly of thiosorbitol are disclosed and claimed in copending application Serial No. 528,179, filed March 25, 1944, by Frank Kerr Signalgo.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claim.

We claim:

A process for plating copper onto a ferrous metal surface which comprises contacting said surface with a heated aqueous solution containing a soluble copper salt of a poly-hydroxythiol, and an acid selected from the group consisting of sulfuric, hydrochloric and phosphoric acids.

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